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The origin and distribution of methane in the Alliston aquifer complex

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1. Introduction

Methane gas seems to be a common trace component in groundwater, and a potentially explosive contaminant where present in high concentration. (Hughes et al. 1971; Coleman, 1976; Barker, 1979). This seems to be the case for groundwater in some parts of the Alliston aquifer complex. Many wells that tap this aquifer produce high volumes of methane. As a result, most of the municipal wells have aeration treatment systems. This aquifer is the major water supply for towns such as Alliston, Cookstowm and Bond Head, and is an essential water resource for a growing population.

The distribution and origin of methane in this aquifer is not well established. Two hypothesis have been postulated. One suggests that the occurrence of methane is controlled by the nature of the underlying Paleozoic bedrock. Where the bedrock is shaley (Collingwood, Blue Mountain Groups), insignificant amounts of methane are found. However, where the bedrock is limestone (Trenton Group), methane is usually found at high concentrations (T.J. Yakutchik, MOE, pers. comm). This implies that the source of methane is leakage or migration from the more permeable limestone bedrock. This hypothesis is encouraged by the fact that methane is likely present in the Trenton Group. It is well documented that these carbonate rocks are an important reservoir for natural gases in other part of southern Ontario. (Barker and Pollock, 1984).

The second hypothesis, based on carbon isotope analyses of methane from overburden wells, suggests that the methane is of biological origin, produced by bacterial action (Barker, Fritz and Brown, 1979; Barker and Fritz, 1981). Consequently, the methane is being generated within the Alliston sand aquifer, as the methane found in the natural gases in the Trenton rocks has a carbon isotopic composition typical of thermocatalytic methane. Therefore, a bedrock control of the occurrence of methane appears to be unlikely.

This paper presents preliminary results from the first stage of an ongoing research project funded by the M.O.E (1987-89), whose main objective is to produce an unified and acceptable theory about the origin of the methane in the Alliston aquifer complex.

2. Hydrogeology

The Alliston Aquifer complex is a confined, discontinuous, but extensive network of fine to gravelly sand lenses underlain by bedrock or basal till and overlain by clayey till. It seems the aquifer complex extends from the vicinity of Aurora to Wasaga Beach and includes the area northwest along Nottawasaga Bay (Figure 1). This information is based on a map of the aquifer complex published by Turner, MOE (1977) and a recent review of water well records filed at the M.O.E offices.

The study area is mostly underlain by rocks of the Simcoe (middle Ordovician) and Nottawasaga (upper Ordovician) Groups. The areal distribution of the various units that form these groups is shown in Figure 2. The units relevant to this study are the Trenton and Black River limestones and the

Collingwood and Blue Mountain shales. In general, the bedrock is not an important source for water supply, and in some areas the water is highly mineralized and not suitable for domestic or stock purposes.

The overburden material that encloses the aquifer complex is of Pleistocene glacial origin and consists of glacio-lacustrine, glacio-fluvial outwash deposits, and ice-deposited drift (till). The stratigraphy of these deposits is extremely variable vertically and laterally. In general, from the bedrock upward, there occur successions of lacustrine and glacio-lacustrine silts and sands, and/or clays with intercalated lenses, fans, or channels of fluvial or glacio-fluvial sands, and /or gravels interlayered with successions of semi-permeable tills. More detailed information about the overburden materials can be found in Sibul and Choo-Ying (1971). High capacity wells have been developed in many part of the aquifer complex. However, high yielding wells often occur at the margins of the complex. Except for the presence of methane and high iron content in some groundwater, the quality of the water is suitable for water supply.

A simplified piezometric surface map is presented in Figure 3. This map is an updated version of Turner (1977) and includes more wells from the margins of the aquifer system in order to better define regions of recharge, specifically in the area south of the complex. The regional groundwater flow pattern illustrates two major flow systems which are separated by a north-south divide at piezometric elevations greater than 750 feet. One dischargs into Nottawasaga Bay to the north and the other to Kempenfelt Bay and Cooks Bay to the northeast. Recharge is regional from the east and west marginal bedrock highs and possibly from the south in the vicinity of Aurora, where there apparently exists an east-west groundwater flow divide.

3. Approach

3.1 Methane origin and distribution

Methane gas (CH_4) is formed by two distinct processes. One process is the decomposition of organic matter by a group of bacteria called Methanogens. This type of methane is referred to as "biogenic methane". The other process is the thermal degradation of organic material during burial and diagenesis. This type of methane is termed "thermocatalytic methane". These processes are accompanied by carbon and hydrogen isotope effects that characterize the methane with a specific isotopic composition that reflects the processes responsible for the methane formation. Biogenic methane, excluding the methane generated in landfills, are characterized by $\delta^{13}C$ values less than -60 o/oo whereas thermocatalytic methane have values greater than about -45 o/oo (Coleman, 1976; Barker and Fritz, 1981). In addition, the hydrogen isotope (deuterium) concentration of biogenic methanes are related to the deuterium concentration of their associated water. This relationship depends on the type of reactions that are involved in the methane formation (CO_2 reduction vs acetate dissimilation) (Shoell, 1980; Woltemate et al, 1984). This study will use carbon-13 and deuterium isotopes as a tracers to provide information about the genesis of the methane.

The distribution of methane in the Alliston aquifer in not well defined. It seems that the area between Bond Head (Beeton), Alliston, Cookstown, and Aurora contains the major occurrence of methane in the groundwater. However, similar occurrences have been noted in the township of Innisfil, and in bedrock wells near Wasaga Beach. Groundwater from overburden and bedrock wells that represent most of the aquifer will be collected for methane analyses. The methane distribution will be compared with the distribution of the various lithologic units that form the underlying bedrock in order to further test the hypothesis of bedrock control on the presence of methane in the groundwater. Additional gas analyses will include hydrocarbon molecules heavier than the methane. The presence of these type of compounds are an indication of the thermocatalytic origin of methane.

3.2 Carbon sources

The occurrence of methane in any type of environment is intimately linked to its carbon precursor, and/or linked to a source rich in organic matter. Potential carbon sources for the generation of methane in the Alliston aquifer complex are organic matter present in the aquifer material and bedrock and dissolved organic carbon (DOC) in the groundwater. The other alternative is migration of methane from hydrocarbon reservoirs that could exist in Paleozoic bedrock. Information about the nature of these sources, specifically its age or time of deposition could be useful in linking the methane to its carbon precursor. Carbon-14 (^{14}C), a radioactive carbon isotope that is widely used for dating of geological materials, will be used as a dating tool in this study. Radiocarbon analyses will be performed on methane samples, on the two main fractions that form DOC (hydrophobic and hydrophilic), and aquifer kerogen if it is available. In addition, geological information related to the time of deposition of the overburden materials and bedrock units are also available in the literature. The geochemical characterization of the DOC will also provide information about the residence time and the organic geochemistry of the groundwater.

3.3 Origin and residence time of the groundwater

One mechanism postulated for methane migration in aquifers is transport as a dissolved solute in groundwater (Coleman, 1976). Therefore, another important aspect of this study is the origin and the residence time (age) of the groundwater. Radiocarbon analyses of dissolved inorganic carbon (DIC) are a common tool used in hydrological studies to provide information about the residence time of the groundwater. However, in aquifers affected by methanogenesis, this method is very imprecise. Efforts will be made to improve the application of DIC radiocarbon dating in these type of aquifers. Furthermore, the stable oxygen-18 (^{18}O) and deuterium (^{2}H) isotopes that form part of the water molecule will be used as a tracers to provide information about recharge environments, and origin of the overburden and bedrock groundwater.

The geochemical information derived from this study, in combination with existing hydrogeological and geochemical data, is expected to provide a unified theory about the origin and distribution of methane in the Alliston aquifer complex. This research should improve the scientific basis for the prediction of other areas of the Alliston aquifer that may be affected with water quality problems associated with the presence of methane. This approach can also be applied to others aquifers contaminated with methane.

4. Preliminary results and discussion

The first step of this project was to compile existing information regarding occurrence of methane and hydrogeological and geochemical aspects of the Alliston aquifer complex (Bliss, M., 1988).

Field work during summer 1988 has focussed mainly on the collection of groundwater and gas samples stripped from groundwater from deep overburden and bedrock wells for isotopic and chemical analyses. The data presented in this

paper corresponds to the southern part of the aquifer complex. The sampling locations can be seen in Figure 4.

4.1 Gas analyses

Chromatographic analyses of gas samples are reported in Table 1. This data shows that the main components of gases extracted from the groundwater are CH_4 and N_2. The average concentration of these two compounds are 80 % and 20% respectively. The samples with high oxygen content indicate air contamination during sampling. No traces of C_2 to C_4 hydrocarbon compounds were found in these samples.

Samples for determination of CH_4 and N_2 concentration were collected in glass syringes and analyzed by gas chromatography. For samples supersaturated with methane (saturation at 25°C is 1310 umol/l), degassing during sampling caused some errors in the determination of gas concentration. All the samples were collected after the pressure tank in domestic wells. Samples with CH_4 levels > 1400 umol/l should be considered with caution. This data is plotted in Figure 4.

It appears that the area southeast of Alliston towards Beeton has high concentrations of methane, either in bedrock or overburden wells. This pattern is not clear in the area northeast of Alliston where bedrock wells contain high concentrations of methane, whereas in nearby overburden wells no gas was observed. No CH_4 was found in overburden and bedrock wells sampled southwest of Alliston.

Table 1 also lists data on dissolved organic carbon (DOC) in the groundwater. A correlation seems to exist between the DOC and CH_4 concentration. High DOG are accompanied by high CH_4 concentrations. Typical DOC concentrations are less than 1 ppm in deep groundwater (Thurman, 1985), and less than 5 ppm in unconfined aquifers in the Alliston area (Wassenaar et al, this volume). These higher DOC concentrations in the Alliston aquifer complex suggest that the groundwater is moving through aquifer materials that are rich in organic matter.

4.2 Isotope analyses

Environmental isotope analyses have been performed by mass spectrometry on methane (^{13}C) and groundwater samples (^{18}O and ^{2}H). The isotope data is expressed in δ o/oo units*. This data is reported in Table 2.

The $\delta^{13}C$ values for methane samples varied between -69 o/oo to -84 o/oo with most of the values around -75 o/oo. No significant isotopic differences have been noted in methane from overburden and bedrock wells. This data is similar to that reported from some overburden wells by Barker and Fritz (1981). Figure 5 shows the $\delta^{13}C$ distribution of methane gases of different origin. This figure does not include the $\delta^{13}C$ values for methane generated in landfill environments, which range between -38 o/oo to -56 o/oo for ^{13}C. All methane results from the Alliston groundwaters plot in the field of biogenic methane.

Stable isotope analyses were also carried out on some overburden and bedrock groundater. This data shows an isotopic range between - 14.3 o/oo and -10.7 o/oo for ^{18}O, and -92 o/oo and - 78 o/oo for ^{2}H. This significant isotopic difference implies that at least two types of groundwater are present in the aquifer. The isotopic composition of modern water in unconfined,

* δ o/oo = $R_s / R_{st} - 1$ * 1000 , where R_s and R_{st} are the isotope ratios ($^{13}C/^{12}C$, $^{18}O/^{16}O$ and $^{2}H/^{1}H$) for the sample and the standard respectively. The international standards used as a reference are PDB (Pee Dee Belemnitella) for ^{13}C and SMOW (Standard Mean Ocean Water), for ^{18}O and ^{2}H.

shallow aquifers in the Alliston area ranges between -10.8 o/oo and -11.5 o/oo for ^{18}O and -78 o/oo and -81 o/oo for ^{2}H (Wassenaar et al, in preparation). Thus, the presence of isotopically depleted groundwaters ($\delta^{18}O$ = -14.3 o/oo) suggest that these waters were recharged under cooler climatic conditions than today.

The preliminary isotopic data gathered suggest that the methane is biogenic in origin and is produced either in the bedrock and/or in the deep overburden materials. Radiocarbon (^{14}C) dating of methane and DOC will provide more information to better define the carbon source for the generation of methane. Major occurrences of methane seem to be found in areas underlain by limestone rocks. However, a bedrock well (386 feet) tapping shale shows the highest level of methane. The relationship between the presence of methane and the nature of the underlying bedrock will be fully tested once the methane distribution in the aquifer is better known.

5. Future work

The main goal of the first stage of this study is to determine methane distribution in the Alliston aquifer complex. Gas and water samples for isotope analyses are also being collected during this stage. Subsequently, selected wells representive of the different geochemical environments that exist in the study area will be used for a complete geochemical evaluation of the following parameters : ^{14}C and ^{13}C in methane, DOC, and DIC; ^{18}O, ^{2}H (methane) and chemistry of the groundwater. Attempts will also be made to study the potential of the kerogen present in the bedrock shales as a carbon source for methane producing bacteria. We will also examine the possibility that methane generation in some parts of the Alliston aquifer complex could be limited by the presence of sulfate-reducing bacteria. Sulfur-34 (^{34}S), a stable sulfur isotope, will be used as a tool to approach this question.

The geochemical information generated from this study will be combined with existing geological and hydrological information to postulate an acceptable theory about the origin and occurrence of methane in the Alliston aquifer complex.

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Table 1. Chemical composition of gas and DOC in water samples, Alliston aquifer complex

Well	Depth ft	CH_4	N_2 %	O_2	CO_2	CH_4 umol/l	N_2	DOC ppm
BR*	198					<20	1180	1.4
OV**	136					<20	1055	3.2
BR	80					<20	1140	0.9
OV	177					<20	800	6.2
OV	55					1455	698	4.2
OV	122					<20	1148	2.0
OV	162					360	750	2.7
OV	176	71.9	27.4	0.50	0.85	2080	510	7.4
OV	234					<20	217	3.3
BR	320	44.2	45.8	7.63	3.70	1515	193	12.6
OV	258					<20		
BR	386	87.8	8.25	0.14	0.91	4680	380	9.3
OV	375	79.8	17.8	0.45	1.13	3550	600	22.0?
OV	281	82.1	13.6	1.25	2.70	2765	335	8.7
BR	245	83.2	13.8	0.3	1.15	2180	248	8.2
OV	194	.				815	667	8.1
OV	190	71.0	29.1	0.55	0.36	2650	737	9.6
BR	305	64.5	35.5	0.80	0.44	2550	977	5.2
OV	262					<20	900	1.7
BR	355	53.1	47.2	0.81	0.18	1413		6.0
OV	367					<20	985	1.9
BR	125	61.3	34.3	3.40	0.17	2425	1000	7.1

* Bedrock
** Overburden

Table 2. Isotopic composition of gas and water samples, Alliston aquifer complex

Well	Depth ft	$\delta^{13}C$ o/oo PDB CH_4	$\delta^{18}O$ o/oo SMOW H_2O	$\delta^{2}H$
BR*	198		-12.8	-89
OV**	177		-11.5	-80
OV	234		-10.8	-78
OV	176	-76.6	-12.2	-83
BR	386	-72.2	-13.8	-100
BR	320	-68.9	-12.3	-88
OV	375	-75.8	-13.5	-92
OV	281	-72.2	-10.9	-78
BR	245	-75.2	-10.7	-79
OV	190	-79.3		
OV	262		-11.6	-80
BR	305	-82.2		
BR	355	-84.5	-14.2	-100
BR	125	-77.0	-12.4	-90

* Bedrock
** Overburden

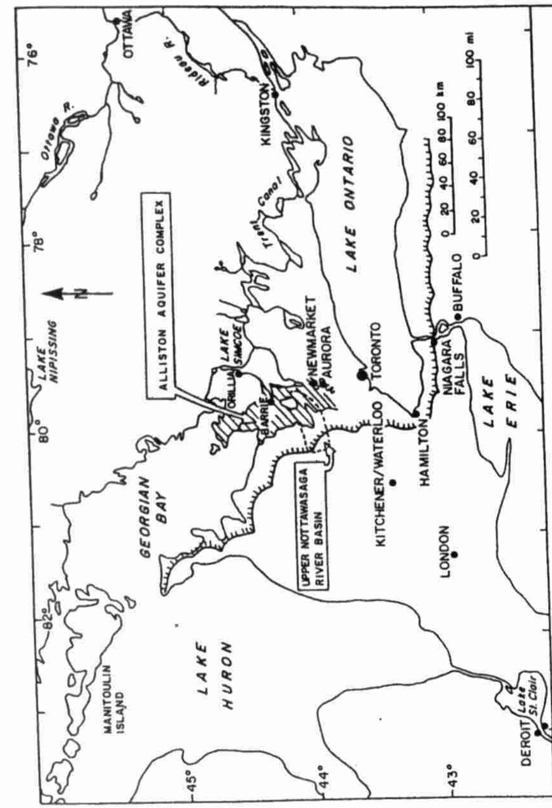

Figure 1. Location map of the study area

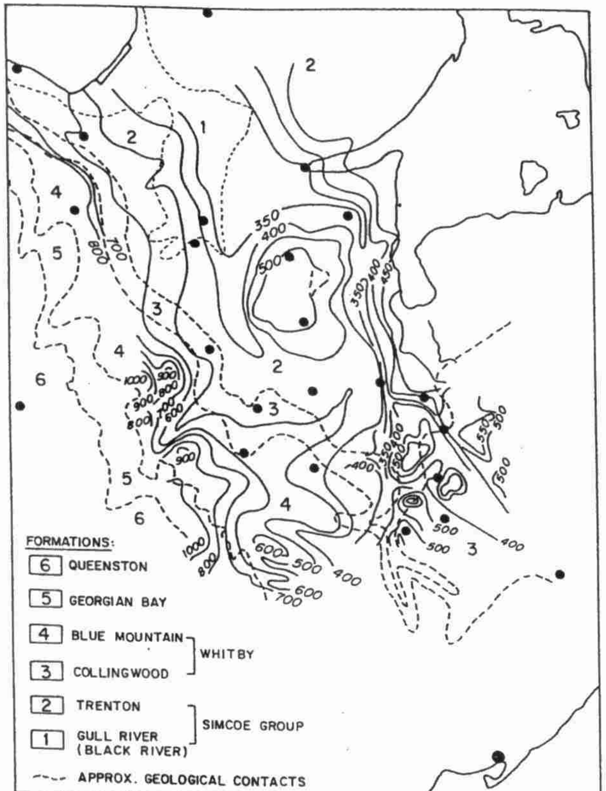

Figure 2. Plan of bedrock topography and lithology

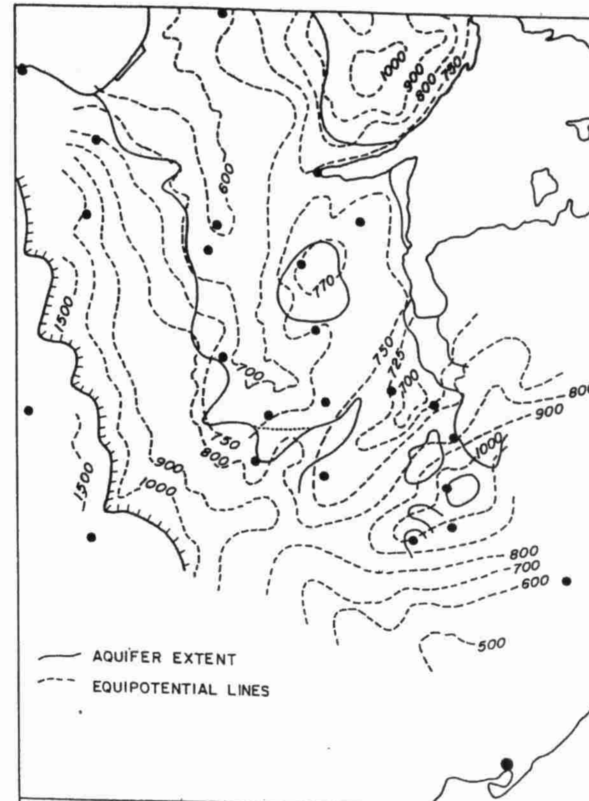

Figure 3: Regional Groundwater Flow Pattern

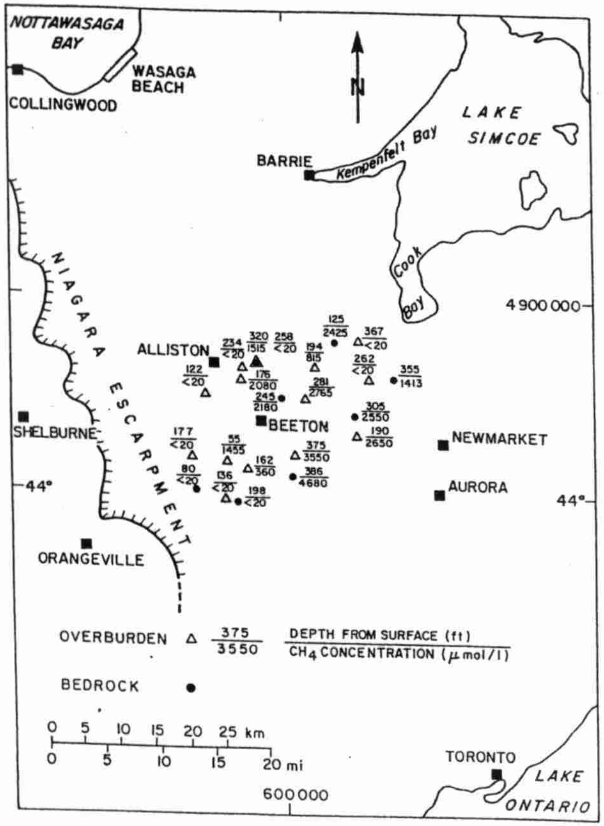

Figure 4. Sampling location and methane concentration in overburden and bedrock wells, Alliston aquifer complex.

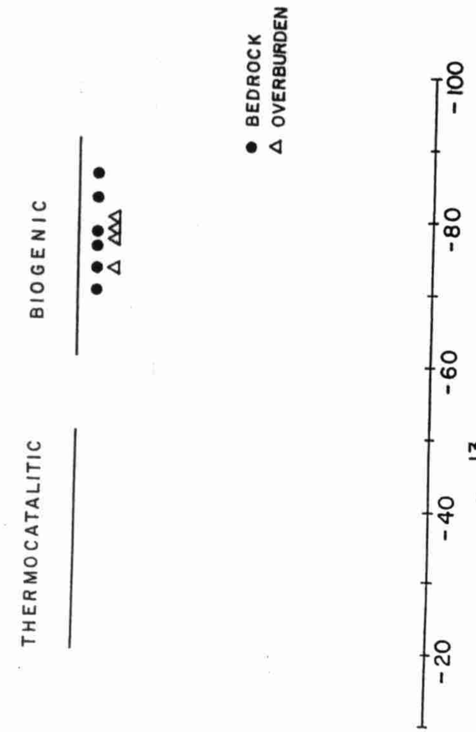

Figure 5. $\delta^{13}C$ distribution of methane of different origin and ^{13}C content in methane from overburden and bedrock wells, Alliston aquifer complex.